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Roles of alkoxy titanates and zirconates as multifunctional agents for polymers*)

Summary — A review discusses the roles of novel alkoxy titanates and zirconates as additives for polymers. As coupling agents, they chemically bond inorganic as well as organic fillers and polymers *via* proton coordination without the need of water of condensation as for alkoxysilanes. Thermally stable alkoxy titanates and zirconates function also as *in-situ* polymerization and copolymerization catalysts for filled or unfilled polymers during the plasticization resulting in their significantly faster thermoplastic processing at lower temperatures. The catalysis effect is permanent even in recycling. Novel trialkoxy zirconates are shown to be transparent, permanent, non-blooming and non-moisture dependent multifunctional agents.

Key words: alkoxy titanates, alkoxy zirconates, adhesion promoters, catalysts, crosslinking agents, mechanical and processing properties of polymers.

The aim of this paper is to discuss a possibility of new thinking of polymer additives art based on organometallic coupling agents, catalysts, and crosslinking agents as taught *via* the six functions of the novel alkoxy titanate and zirconate molecules presented recently by Monte [1]. He has compared their structures and properties with the traditional alkoxysilane ones and has shown what alkoxysilane based coupling agents could do and what their limitations were as it related to reactable fillers such as calcium carbonate, carbon black and organic substrates.

COUPLING

Organosilanes have long been used to enhance the chemical bonding of a variety of thermoset polymers with siliceous surfaces of the fillers [1]. However, organosilanes do not function as coupling agents for carbon black, calcium carbonate, boron nitride, and graphite particles or aramid and other organic derived fibers [2].

To explain the performance differences between titanates or zirconates and silanes, a discussion may be represented as follows [1]:

alkoxy titanates (zirconates)

$$\overset{(1)}{[\mathrm{RO}-]}_n\overset{(2)}{\mathrm{Ti(Zr)}}[-\overset{(3)}{\mathrm{O}}\overset{(4)}{\mathrm{X}}\overset{(5)}{\mathrm{R'}}\overset{(6)}{\mathrm{Y}}]_{4-n} \qquad (I)$$

alkoxysilanes

$$\overset{(1)}{[\mathrm{RO}-]}_3\mathrm{Si}[-\overset{(5)}{\mathrm{R'}}\mathrm{Y}] \qquad (II)$$

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In Formula (I) and (II) RO (1) is hydrolyzable or substrate reactive group with surface hydroxyl or protons.

Ti, Zr, Si (2) are tetravalent titanium, zirconium or silicon. Ti–O or Zr–O bonds are capable to disassociate allowing transesterification, transalkylation, and "repolymerization" (see the further sections) reactions while Si–C bond is more stable and thus unreactive.

X (3) represents the binder functional groups such as phosphato-, pyrophosphato-, sulfonyl, carboxyl, *etc.* which impart *e.g.* burn rate control or anticorrosion properties of a material as well as quarternization sites and disassociation rate or electron transfer control.

R′ (4) is thermoplastic functional aliphatic and nonpolar (*e.g.* isopropyl, butyl, octyl), naphtenic and middly polar (*e.g.* dodecylbenzyl) or aromatic (*e.g.* phenyl, benzyl, cumyl) group.

Y (5) is thermoset functional group such as acryl, methacryl, thio-, amino-, *etc.*

4 - n (6) represents mono-, di- or tri-organofunctionality.

The function (1) represents a coupling action. Its mechanism may be conditioned by a proton reactive in the case of titanates or zirconates, *via* solvolysis or coordination without the need of water of condensation, and hydroxyl group reactive in the case of silanes, *via* a silanol-siloxane mechanism requiring water of condensation. Functions (2) to (6) are polymer curative reactive. The coupling of titanates or zirconates to the inorganic or organic substrate in atomic monolayers allows to form the completely continuous phase for stress/strain transfer.

To the perfect localization and absorption of the coupling agent on the substrate, the coupling agents physical forms like polymers physical forms are recommended to be used: LICA (LIquid Coupling Agent) for liquid polymers, CAPOW (Coupling Agent POWder) for powder polymers, and CAPS (Coupling Agent Pellet System) for pelleted polymers.

Chemistry of coupling is as important as physics of mixing. Figure 1, as an example, compares the effect of 2-propanolato-tris(isooctadecanoato) titanate (KR TTS) with the effect of a conventional wetting agent (zinc stearate) on mixing torque of low density polyethylene (PE-LD) filled with calcium carbonate [1]. It is clear from it that KR TTS shows much more significant effect resulting in lower viscosity of the polymer mixture and thus in its better processability.

CATALYSIS

Organic titanates and zirconates are well known catalysts used in the manufacture of polyolefins, polyesters, poly(butylene terephthalate), polyurethanes, polycarbonates, and polysiloxanes [1, 3—7]. The coordinate titanates are shown to improve the colour and appearance of the basic polymers [1].

New polymers synthesized in the presence of titanocene or zirconocene catalysts exhibit superior flow and improved strain properties as compared with analogous polymers synthesized in the presence of Ziegler—Natta catalysts [8]. This catalysis called by Monte [1] as "metallocene-like" has been termed "repolymerization" [9]. Of course, it is really neither metallocene-like, nor repolymerization (see the next section), but brings novel rheology and stress/strain effects in thermoplastics and thermosets independently on crosslinking and curative effects. The titanocene or zirconocene catalysts used do not remain in the polymer. Using this process, thermoplastics may be regenerated to virgin or recycled ones. It appears to influence the isothermal recrystallization time, chain branching and morphology of the polymer chains surrounding the particle or fiber. The catalysis benefits thus lead to an easier processing and better me-

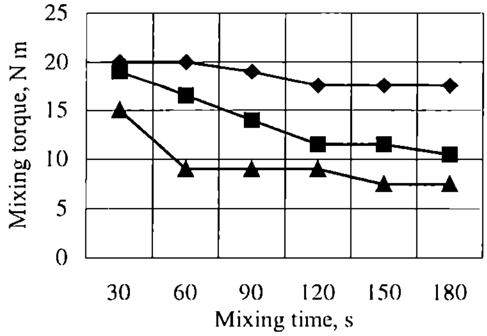

Fig. 1. Effects of additions (2 wt. %) of 2-propanolato-tris(isooctadecanoato) titanate (▲) and zinc stearate (■) on the mixing torque (rotor speed 82 min^{-1}, temperature 93 °C) of calcium carbonate filled (7 wt. %) low density polyethylene (◆)

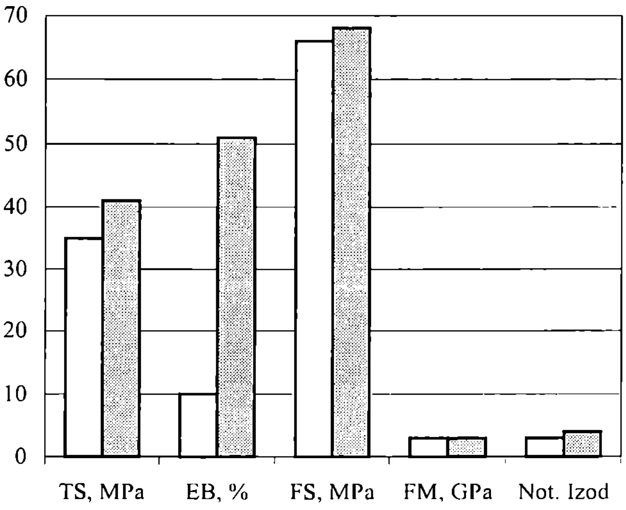

Fig. 2. Effects of 2,2-bis(2-propenolatomethyl)-butanolato-tris(dioctyl)phosphato titanate (0.3 wt. % of polymer in CAPOW form) (■) on tensile strength (TS), elongation at break (EB), flexural strength (FS), flexural modulus (FM), and Izod notched impact strength (not. Izod) values of injection molded unfilled polystyrene (□)

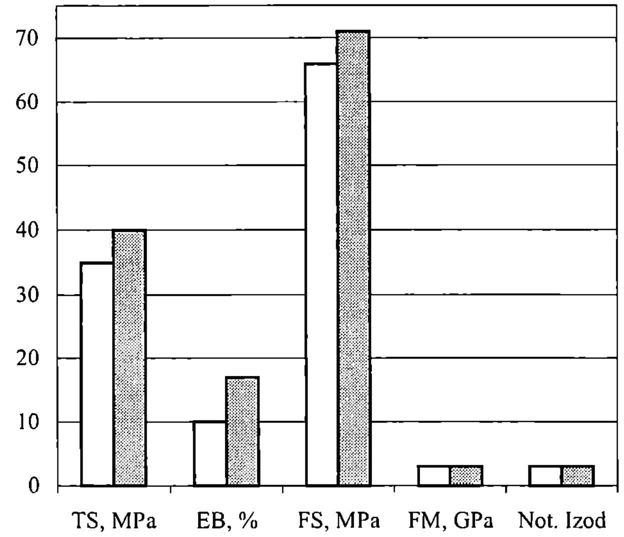

Fig. 3. Effects of 2,2-bis(2-propenolatomethyl)-butanolato-tris(dioctyl)phosphato zirconate (0.3 wt. % of polymer in CAPOW form) (■) on the mechanical properties (as in Fig. 2) of injection molded unfilled polystyrene (□)

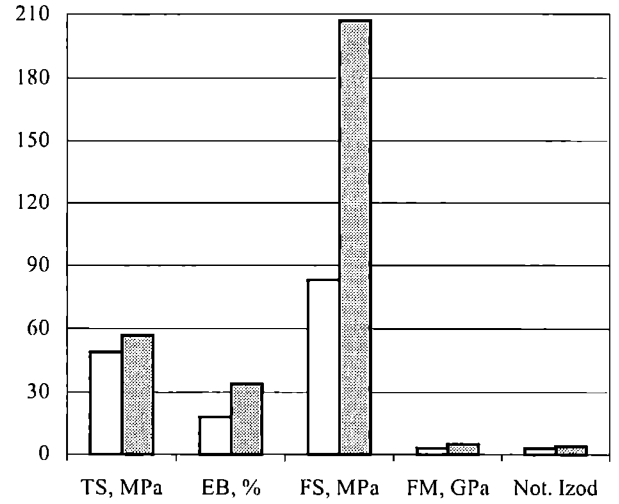

Fig. 4. Effects of 2,2-bis(2-propenolatomethyl)-butanolato-tris(dioctyl)phosphato zirconate (0.3 wt. % of polymer in CAPOW form) (■) on the mechanical properties (as in Fig. 2) of injection molded unfilled acrylonitrile-butadiene-styrene copolymer (□)

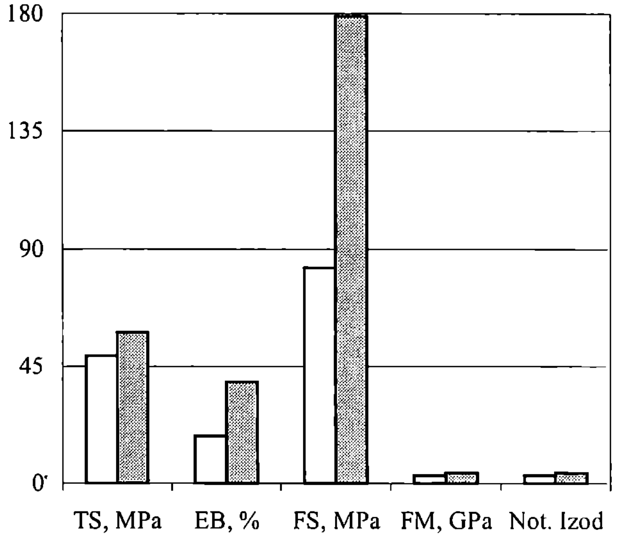

Fig. 5. Effects of 2,2-bis(propenolatomethyl)-butanolato-tris(dioctyl)phosphato titanate (0.3 wt. % of polymer in CAPOW form) (■) on the mechanical properties (as in Fig. 2) of injection molded unfilled acrylonitrile-butadiene-styrene copolymer (□)

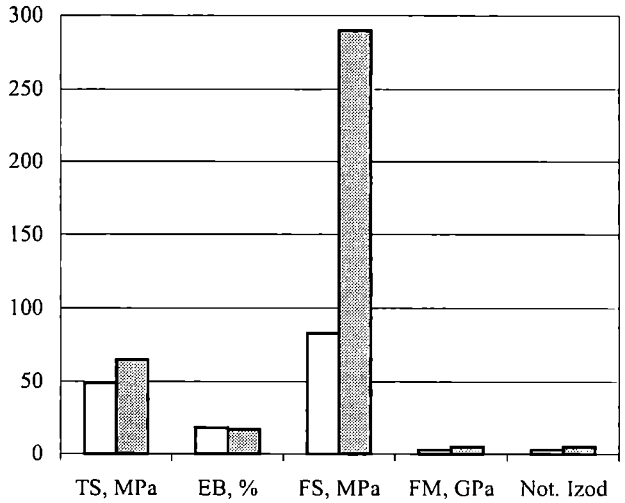

Fig. 6. Effects of 2,2-bis(propenolatomethyl)-tris(2-ethylenediamino)ethylato titanate (0.3 wt. % of polymer in CAPOW form) (■) on the mechanical properties (as in Fig. 2) of injection molded unfilled acrylonitrile-butadiene-styrene copolymer (□)

chanical properties. Figures 2—6 illustrate the effects of some alkoxy titanates and zirconates on mechanical properties of injection molded unfilled polystyrene (PS) and acrylonitrile-butadiene-styrene copolymer (ABS). In the case of PS, an addition of a titanate increases mainly elongation at break (Fig. 2). The same addition of a zirconate influences elongation at break as well, and also significantly flexural strength (Fig. 3). In the case of ABS, similar effects can be seen in Figs. 4—6 (Figures 2—6 based on the data from [1]).

MACROMOLECULAR MODIFICATIONS

In the presence of two or more (different) polymers (in the absence or presence of inorganic or organic fillers), "repolymerization" manifests itself as copolymerization, grafting or other macromolecular modification. Titanate and zirconate coupling agents may act as compatibilizers *via* activation of both addition and condensation polymers [10].

Moreover, these organometallic compounds are effective esterification catalysts in the polyester macromolecular melt [1].

CROSSLINKING

According to Monte [1], titanates and zirconates are able to cause effectively the crosslinking of a very broad gamut of polymers including polyolefins, polybutadienes, styrene-butadiene copolymers, polystyrene, polysiloxanes, epoxy resins, fluorocarbon polymers, acrylic and methacrylic resins, poly(vinyl alcohol), and others. However, Monte has shown only one example [11]: ethylene-vinyl acetate copolymer has been crosslinked with a neoalkoxy trimethacryl zirconate in the presence of 0.5 phr of dicumyl peroxide, when immersed in water at 25 °C for 72 hours.

On the other hand, conclusion of a paper [12] cited by Monte [1] as ref. 42 is as follows: "A series of composites based on a commercial SBS block copolymer sample and clays was prepared using KR TTS, as coupling agent. The composites prepared using the surface modified clays present lower torque and temperature of mixing than the analogous composites prepared without the coupling agent. Accordingly, better processability of the final compounds results from the use of coupling agents. No side reactions, such as crosslinking reactions, were observed during processing and, accordingly, the thermoplastic character of the SBS is fully retained also in the composites". Thus one can ask if the novel alkoxy titanates and zirconates really are able to act as crosslinking agents or as co-agents only.

CONCLUSIONS

Novel alkoxy titanates and zirconates as coupling agents chemically bond inorganic as well as organic fillers and polymers *via* proton coordination without the need of water of condensation.

Thermally stable alkoxy titanates and zirconates function as *in-situ* polymerization and copolymerization catalysts for filled or unfilled polymers during the plasticization resulting in significantly faster thermoplastics processing at lower temperatures. The catalysis effect is permanent even in recycling.

Their role as crosslinking agents for a broad family of polymers is questionable.

Novel trialkoxy zirconates are shown to be transparent, permanent, non-blooming and non-moisture dependent multifunctional agents.

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